

Ligand Substitution Processes on Carbonylmetal Derivatives. 4.¹ NMR Study of the Reaction of Hydridocarbonylchromates with PX₃ (X = Br, Cl)[†]

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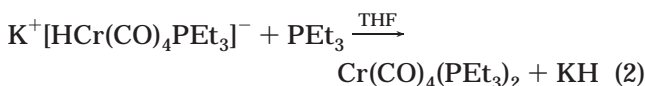
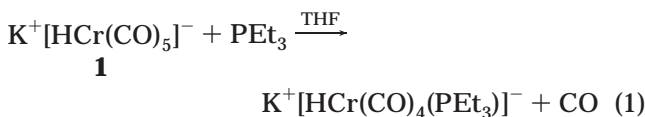
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Summary: At 193 K, K⁺[HCr(CO)₅]⁻ (1 equiv) reacts with PBr₃ to give Cr(CO)₅PH₃ and K⁺[BrCr(CO)₅]⁻. The latter further reacts with PBr₃ only above 253 K to give Cr(CO)₅PBr₃. At room temperature, K⁺[HCr(CO)₅]⁻ (3 equiv) reacts with PBr₃ to give Cr(CO)₅PH₃ as the sole phosphorus derivative. A similar reactivity is observed for the reaction of K⁺[HCr(CO)₅]⁻ with PCl₃. In contrast, K⁺(μ-H)[Cr(CO)₅]₂⁻ reacts with PBr₃ only above 298 K, affording selectively Cr(CO)₅PBr₃.

Ligand substitution processes in transition metal complexes, especially neutral metal carbonyls, have attracted much attention, both for the design of specific syntheses of heteroleptic complexes and for a contribution to the understanding of reaction mechanisms, particularly the loss of small molecules or ions from low-valent metal complexes.^{2–4}

In the last years, our study of ligand substitution processes on K⁺[HFe(CO)₄]⁻ has been particularly fruitful, both from a synthetic point of view and for the understanding of the reactivity of hydridocarbonylferates toward phosphites and phosphines.⁵

More recently we reported a study of the reaction of phosphines with the chromium derivative K⁺[HCr(CO)₅]⁻, **1**, in aprotic solvents.¹ The reaction of **1** with PEt₃ starts by a carbonyl ligand substitution, generating the monosubstituted derivative K⁺[HCr(CO)₄PEt₃]⁻. Although the latter complex could be spectroscopically characterized, it reacts in situ with the PEt₃ to afford the disubstituted *trans*-Cr(CO)₄(PEt₃)₂ complex by displacement of the hydride ligand (eqs 1, 2).

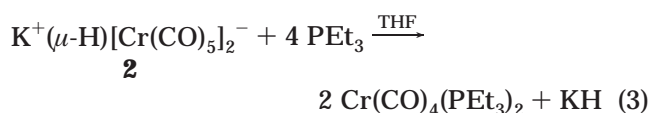


The bridged dinuclear hydride K⁺(μ-H)[Cr(CO)₅]₂⁻, **2**, also reacts with PEt₃ to give *trans*-Cr(CO)₄(PEt₃)₂ (eq 3).^{1,6}

[†] Dedicated to Professor J. Barrans on the occasion of his 70th birthday.

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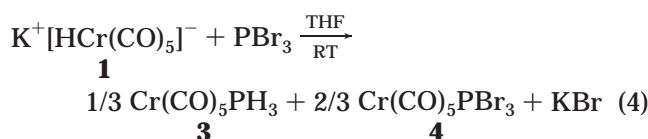
(1) Part of the Ph.D. Thesis of E. Roblou. For Part 3, see: Brunet, J.-J.; Diallo, O.; Donnadieu, B.; Roblou, E. *Organometallics* **2002**, *21*, 3388–3394.



Thus, although different mechanisms are involved,¹ the reactions of **1** and **2** with PEt₃ yield the same disubstituted *trans*-Cr(CO)₄(PEt₃)₂ derivative.

In this communication, we wish to report for the first time the reactions of **1** and **2** with trihalogenophosphines, PX₃ (X = Br, Cl), evidencing a great difference of reactivity between these two hydridocarbonylmetalates.

When **1** was reacted with 1 equiv of PBr₃ in THF at RT for 3 h in a Schlenk tube, a mixture of two new phosphorus complexes is formed which exhibits ³¹P{¹H} NMR signals at δ = -127.7 and 95.8 ppm (ca. 1:2 ratio). PBr₃ (δ = 233.8 ppm) was totally consumed. According to the assignments determined later (vide infra), this reaction can be represented by eq 4.



To gain more information, the reaction of **1** with PBr₃ was performed at low temperature in THF-*d*₈ in a NMR tube and monitored by ³¹P and ¹H NMR. After mixing the precooled reagents (1:1) at ca. 100 K, the temperature of the probe was allowed to reach 193 K. After 0.5 h, the ³¹P NMR spectrum indicated the presence of unreacted PBr₃ (major compound) and of a unique new phosphorus compound, **3**, exhibiting a well-defined quadruplet at δ = -127.7 ppm (¹J_{P-H} = 344 Hz). No trace of free PH₃ (δ_P = -242.4 ppm) could be detected. The ¹H NMR spectrum indicated the total consumption of **1** (δ = -6.9 ppm) and the appearance of a doublet at δ = 3.8 ppm (¹J_{H-P} = 344 Hz) corresponding to **3** (a small

(2) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1968. Basolo, F. *Inorg. Chim. Acta* **1981**, *50*, 65–70.

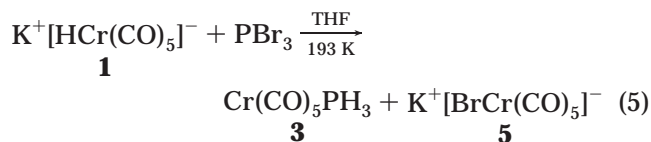
(3) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227–259. Luth, T. Y. *Coord. Chem. Rev.* **1984**, *60*, 255–276.

(4) Darensbourg, D. J. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West R., Eds.; Academic Press: New York, 1982; Vol. 21, pp 113–150.

(5) Brunet, J.-J.; Chauvin, R.; Diallo, O.; Kindela, F.-B.; Leglaye, P.; Neibecker, D. *Coord. Chem. Rev.* **1998**, *178–180*, 331–351.

(6) Darensbourg, M. Y.; Walker, N.; Burch, R. R. *Inorg. Chem.* **1978**, *17*, 52–56.

signal corresponding to **2** ($\delta = -19.5$ ppm) is also observed). Examination of literature data led us to conclude that **3** was the previously reported monosubstituted complex $\text{Cr}(\text{CO})_5\text{PH}_3$.⁷ This assignment was confirmed by the ^{13}C NMR spectrum of the reaction mixture at 193 K.⁸ Interestingly, the above ^{13}C NMR spectrum also indicates the presence of $\text{K}^+[\text{BrCr}(\text{CO})_5]^-$, **5**, and of small amounts of **2**, both identified by comparison with the ^{13}C NMR spectra of authentic samples registered at 193 K.⁹ Furthermore a very minor signal is observed at $\delta = 215.5$ ppm. The latter does not correspond to $\text{Cr}(\text{CO})_5\text{thf}$ ¹⁰ and may be tentatively assigned to $\text{K}^+(\mu\text{-Br})[\text{Cr}(\text{CO})_5]_2^-$.¹³ These observations are *qualitatively* summarized by eq 5.



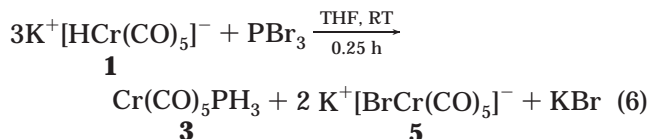
Since the reaction did not seem to evolve at 193 K, the temperature was allowed to increase slowly. ^{31}P NMR monitoring allowed the observation of the formation of a new phosphorus complex, **4** ($\delta = 95.8$ ppm, s), starting when the temperature reached ca. 255 K, whereas the consumption of **2** apparently occurred only after reaching 273 K (^1H NMR analysis). Consumption of PBr_3 was complete at 293 K. The ^{31}P NMR chemical shift of **4** corresponds to that of the monosubstituted $\text{Cr}(\text{CO})_5\text{PBr}_3$ derivative.¹⁴ This assignment was confirmed by recording the ^{13}C and $^{13}\text{C}\{^{31}\text{P}\}$ NMR spectra of pure **4** (vide infra), which exhibits two doublets (ca. 1:4 ratio) ($\delta_{\text{trans-CO}} = 217.8$ ppm, d, $^2J_{\text{C-P}} = 5$ Hz, and $\delta_{\text{cis-CO}} = 213.3$ ppm, d, $^2J_{\text{C-P}} = 14$ Hz), in agreement with literature data.¹⁴

It thus appeared that **1** reacts with PBr_3 at 193 K to give selectively **3**, with formation of unsaturated “ $\text{Cr}(\text{CO})_5$ ” species, stabilized mainly as **5**. In contrast, in situ generated **2** does not react with PBr_3 at 193 K. The reaction starts only at higher temperatures to give $\text{Cr}(\text{CO})_5\text{PBr}_3$, **4** (and perhaps some amounts of **3**). Furthermore, it could be anticipated that PBr_3 reacts with $\text{K}^+[\text{BrCr}(\text{CO})_5]^-$ near 255 K, affording **4**.

To verify the above hypothesis, we examined the reaction of PBr_3 with **5**.¹⁵ The reaction of PBr_3 with **5**

(1 equiv) in THF was started at 193 K and monitored by ^{31}P NMR. As expected, no reaction occurred at this temperature. Allowing the temperature to increase slowly promoted the formation of **4** near 255 K, thus confirming our previous expectations. The consumption of PBr_3 was complete after a few hours at 298 K.

Owing to the formation of $\text{Cr}(\text{CO})_5\text{PH}_3$ (eq 1), we also adapted the stoichiometry for the reaction of **1** with PBr_3 . Reacting PBr_3 with 3 equiv of **1** in THF- d_8 at RT for 0.25 h promoted the total consumption of **1** (^1H NMR analysis) and the formation of **3** as the sole phosphorus complex (^{31}P NMR analysis), thus suggesting a quantitative transformation (eq 6). The liberated “ $\text{Cr}(\text{CO})_5$ ” moiety is stabilized as **5** (^{13}C NMR analysis).



To try to detect some intermediate species, reaction 6 was performed using a large (100 fold) excess of PBr_3 . Unfortunately, even at 193 K, no intermediate could be evidenced. In particular, no trace of free PH_3 could be detected. Consequently, we also examined the reaction of PH_3 with **5**. Bubbling slowly gaseous PH_3 ¹⁸ into a THF solution of **5** at 193 K clearly indicated (^{31}P NMR and IR monitoring) that no reaction occurred at this temperature. The reaction of PH_3 with **5** started only when the temperature reached 293 K, generating **3** selectively. It thus appears that the formation of **3** at 193 K (reaction 5) does not involve free PH_3 .

Although a little less reactive than PBr_3 , PCl_3 similarly reacts with **1** to give **3**. Interestingly, however, when the reaction of **1** with a 100-fold excess of PCl_3 was conducted in *toluene* at RT, ^{31}P and ^1H NMR analyses allowed the observation of two intermediate carbonylchromium complexes, $\text{Cr}(\text{CO})_5\text{PHCl}_2$ and $\text{Cr}(\text{CO})_5\text{PH}_2\text{Cl}$.¹⁹ This result confirms that PH_3 is not formed before complexation on the carbonylchromium species and strongly suggests that the reaction starts by a tandem reduction–complexation of PCl_3 generating $\text{Cr}(\text{CO})_5\text{PHCl}_2$, which is further reduced, step by step, to $\text{Cr}(\text{CO})_5\text{PH}_3$.

For comparison, we also examined the reaction of **2** with PBr_3 . Adding PBr_3 (1 equiv) to a THF- d_8 solution of **2** at 193 K in a NMR tube confirmed that **2** does not react with PBr_3 at this temperature (^{31}P NMR analysis). The reaction started only when the temperature reached 293 K, affording selectively **4** (no trace of **3**). PBr_3 was

(7) The reported ^{31}P NMR chemical shift for **3** is $\delta_{\text{P}} = -129.6$ ppm. The disubstituted $\text{cis-Cr}(\text{CO})_4(\text{PH}_3)_2$ has also been described ($\delta_{\text{P}} = -121.5$ ppm, $\delta_{\text{H}} = 3.7$ ppm, $^1J_{\text{H-P}} = 317$ Hz). Moser, E.; Fischer, E. O.; Bathelt, W.; Gretner, W.; Knauss, L.; Louis, E. *J. Organomet. Chem.* **1969**, *19*, 377–385.

(8) The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** exhibits two doublets in a 1:4 ratio ($\delta_{\text{trans-CO}} 221.6$ ppm, $^2J_{\text{C-P}} = 6$ Hz and $\delta_{\text{cis-CO}} 216.6$ ppm, $^2J_{\text{C-P}} = 14$ Hz).

(9) ^{13}C NMR for **5** (THF- d_8 at 193 K): $\delta_{\text{trans-CO}} 225.0$ ppm and $\delta_{\text{cis-CO}} 217.2$ ppm. ^{13}C NMR for **2** (THF- d_8 at 193 K): $\delta_{\text{trans-CO}} 226.1$ ppm and $\delta_{\text{cis-CO}} 221.3$ ppm.

(10) The ^{13}C NMR data of $\text{Cr}(\text{CO})_5\text{thf}$ have never been reported, probably because of its high instability in solution.¹¹ A solution of $\text{Cr}(\text{CO})_6$ in THF- d_8 was irradiated for 1 h at $\lambda = 365$ nm. The IR spectrum of the above solution exhibits the expected main absorption bands (1936 and 1894 cm^{-1})¹² together with that of unreacted $\text{Cr}(\text{CO})_6$ (1977 cm^{-1}). The solution was immediately cooled to ca. 193 K and the ^{13}C NMR spectrum recorded at 193 K for 3 h. It exhibits signals at $\delta 212.9$ ppm ($\text{Cr}(\text{CO})_6$) and $\delta 220.8$ ppm, tentatively assigned to the cis-CO of $\text{Cr}(\text{CO})_5\text{thf}$.

(11) Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65–71.

(12) Arndt, L. W.; Bischoff, C. J.; Darenbourg, M. Y. *Inorg. Synth.* **1989**, *26*, 335–341.

(13) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1821–1825.

(14) Davies, M. S.; Pierens, R. K.; Aroney, M. J. *J. Organomet. Chem.* **1993**, *458*, 141–146.

(15) Although $[\text{XCr}(\text{CO})_5]^-$ derivatives have been known for long time,¹⁶ the potassium salt $\text{K}^+[\text{BrCr}(\text{CO})_5]^-$, **5**, has never been described. Its preparation was adapted from that of $\text{Et}_4\text{N}^+[\text{BrCr}(\text{CO})_5]^-$ by reacting **1** with CHBr_3 in THF.¹⁷ ^{13}C NMR spectrum of **5** at 193 K (THF- d_8): 2 signals in 1:4 ratio, $\delta_{\text{trans-CO}} 225.0$ ppm and $\delta_{\text{cis-CO}} 217.2$ ppm.

(16) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068–2070.

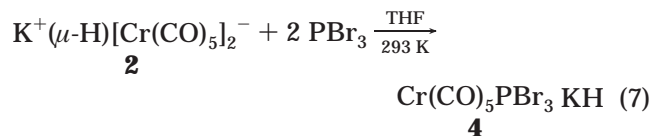
(17) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *Organometallics* **1982**, *1*, 679–681.

(18) PH_3 was generated by reaction of PCl_3 with LiAlH_4 according to: Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779–783.

(19) NMR data (toluene- d_8) for $\text{Cr}(\text{CO})_5\text{PHCl}_2$: ^{31}P , $\delta 158.8$ ppm, d, $^1J_{\text{P-H}} = 402$ Hz; ^1H , $\delta 7.63$ ppm, d, $^1J_{\text{H-P}} = 402$ Hz, in agreement with literature data.²⁰ NMR data (toluene- d_8) for $\text{Cr}(\text{CO})_5\text{PH}_2\text{Cl}$: ^{31}P , $\delta 51.2$ ppm, t, $^1J_{\text{P-H}} = 356$ Hz; ^1H , $\delta 5.68$ ppm, d, $^1J_{\text{H-P}} = 356$ Hz.

(20) Bartmann, A.; Diemert, K.; Kuchen, W. *J. Organomet. Chem.* **1993**, *453*, 65–70.

totally converted after 10 h at 293 K, whereas large amounts of **2** were still present. As expected, reacting **2** with 2 equiv of PBr₃ for 23 h at RT (eq 7) induced complete consumption of PBr₃ with formation of **4** as the sole carbonylchromium complex (¹³C NMR analysis).



It is thus clear that **1** and **2** react quite differently with PX₃. The reaction of **1** may be viewed as a fast tandem reduction–complexation of PX₃ by the hydride, generating Cr(CO)₅PHX₂, which is further reduced by **1**, to finally afford Cr(CO)₅PH₃. The liberated “Cr(CO)₅” species are stabilized as K⁺[XCr(CO)₅]⁻.

In contrast, **2** does not react with PBr₃ as a hydride transfer agent. Therefore, it would be expected to react

like classical phosphines. Under the same conditions, **2** has been shown to react with PEt₃ to afford the disubstituted derivative Cr(CO)₄(PEt₃)₂, a reaction that involves the substitution of both a CO *and* the hydride ligand.^{1,6} The reaction of **2** with PBr₃ involves a completely different mechanism. Indeed, no CO substitution is observed in the final product, and the in situ disruption of **2** into “Cr(CO)₅” and [HCr(CO)₅]⁻ is highly doubtful since the latter would have reacted with PBr₃ to give Cr(CO)₅PH₃ and Cr(CO)₅PBr₃ according to eq 4.

Work is in progress to gain more insight into the reaction mechanism of K⁺(μ-H)[Cr(CO)₅]₂⁻ with trihalophosphines.

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